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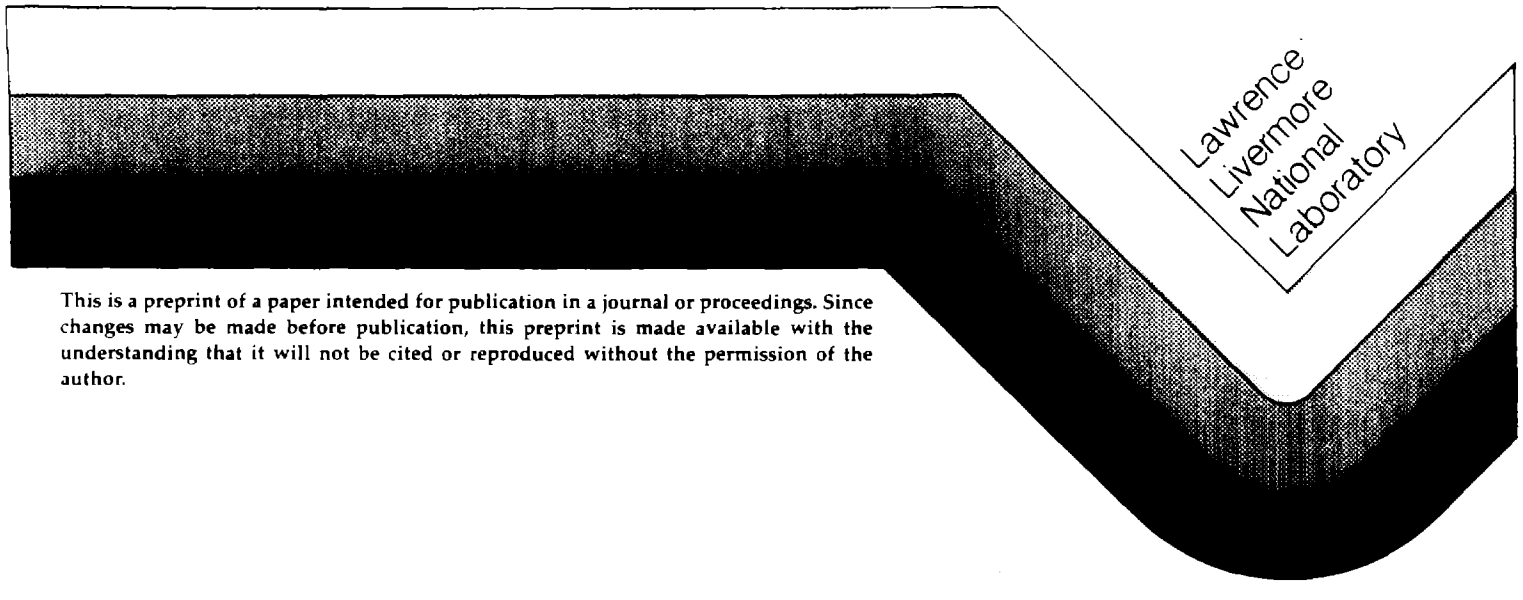

FIRST-PRINCIPLES EQUATIONS OF STATE FOR Al, Cu, AND Pb IN THE PRESSURE RANGE 1-10 MBAR

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Utilizing quantum-mechanical calculations of electronic structure and interatomic forces, first-principles equations of state for the metals Al, Cu, and Pb have been constructed and applied to the analysis of recent shock-impedance-match experiments below 25 Mbar, in which Al served as the reference material.

Accurate equation-of-state (EOS) information is often important in the interpretation of dynamic as well as static high-pressure experiments. Shock-impedance-match experiments, for example, provide EOS data on a given sample *relative* to a second reference material. The EOS one thereby infers for the sample is only as good as one's knowledge of the EOS of the reference. Likewise, in diamond-anvil-cell (DAC) measurements, accurate calibration is required to assign correct values to the pressure. Current DAC calibration schemes are based upon shock-reduced room-temperature isotherms below 2 Mbar. With the recent experimental trend towards ultra-high pressures above 2 Mbar has come the need for accurate EOS data under extreme conditions. This has enhanced the importance of theory in interpreting shock-wave experiments because thermal pressures along the Hugoniot are no longer small nor readily approximated by simple models in this regime. In the present paper, we report new first-principles equations of state for the metals Al, Cu, and Pb above 1 Mbar and up to at least 10 Mbar in each case. All three of these metals are potential EOS standards, and we apply our results here to analyze recent nuclear-driven shock-impedance-match experiments below 25 Mbar,[1,2] in which Al served as the reference material and Cu and Pb were among the samples investigated.

In the pressure range 1-10 Mbar, shock temperatures in Al, Cu, and Pb never exceed one-third of the Fermi temperature T_F. The electrons, therefore, remain substantially degenerate and the usual low-temperature expansions of condensed-matter physics represent a good starting point to describe their behavior. On the other hand, the onset of melting on the shock Hugoniot is predicted to occur at 1.2 Mbar in Al,[3] at 2.3 Mbar in Cu,[4] and at 0.5 Mbar in Pb,[5] so that the energetics of ion motion relevant to both the solid and to the hot liquid metal are of interest here. We have developed a theoretical approach which both satisfies these requirements and allows us to use local-density-functional quantum mechanics[6] in obtaining the EOS under such conditions. In this scheme, the total pressure in the metal is partitioned into zero-temperature, ion-thermal, and electron thermal components according to

$$P(\Omega,T) = P_0(\Omega) + P_{ion}(\Omega,T) + P_{el}(\Omega,T). \quad (1)$$

This separation of terms allows one to directly utilize first-principles energy-band results for the T=0 component P_0. In the present work, these have been obtained for the fcc solid from nonrelativistic augmented-plane-wave calculations in the cases of Al[7] and Cu[8] and from our own semirelativistic linear-

muffin-tin-orbital calculations in the case of Pb.[5]

The ion-thermal component P_{ion} is obtained from first-principles generalized pseudopotential theory (GPT).[3-5,9] The GPT accomodates the energetics of ion motion for both simple nearly-free-electron metals (e.g., Al), as do conventional pseudopotential methods, and *d*-band metals (e.g., Cu), which conventional methods can not treat. In real space, the GPT provides a structure-independent interatomic potential which applies equally to the solid or the liquid at a given volume. Ion-thermal pressures are then calculated from these potentials using quasi-harmonic lattice dynamics in the solid and variational perturbation theory based on a soft-sphere reference system[10] in the liquid.

The additional electron-thermal component P_{el} is obtained from the usual T^2 correction term below 0.1 T_F and from a parameter-free, hot-compressed-atom model[11] above 0.1 T_F. The latter model also has the advantage here of applying equally to both simple and *d*-band metals.

The relative contributions of P_0, P_{ion}, and P_{el} to the total Hugoniot pressure above 1 Mbar is illustrated in Fig. 1 for the case of Al. Near 1 Mbar on the Hugoniot, P_0 is the dominant component of the pressure, accounting for 75% of the total, while the remaining 25% is mostly taken up by P_{ion}. Under increasing compression, the magnitude of P_0 increases, but its percentage contribution steadily drops and near 15 Mbar on the Hugoniot is only 40% of the total pressure. The thermal components, on the other hand, increase both in magnitude and percentage of the total. Near 15 Mbar, P_{ion} is also 40% of the total pressure, while P_{el} accounts for the remaining 20%.

In an *absolute* shock-wave experiment, both the shock velocity u_s and the particle or mass velocity u_p are measured quantities, and the

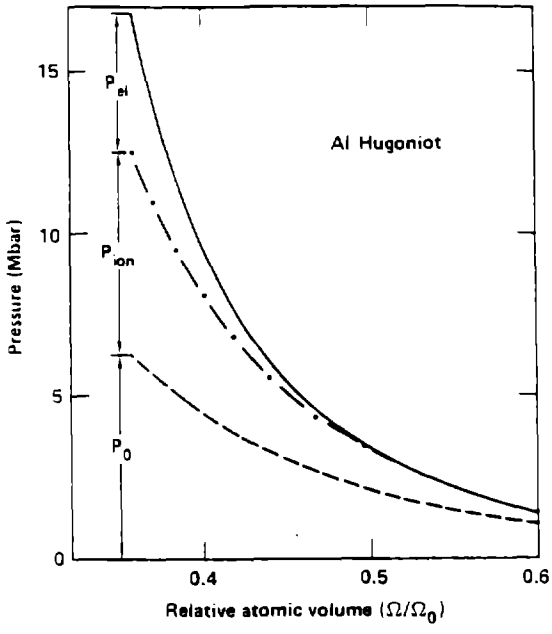

FIGURE 1
Total Hugoniot pressure and its zero-temperature (P_0), ion-thermal (P_{ion}), and electron-thermal (P_{el}) components for Al.

pressure P and density ρ or volume Ω of the shocked state can be calculated from the usual Hugoniot conservation relations:

$$P = \rho_0 u_s u_p \qquad (2)$$

and

$$\rho_0/\rho = \Omega/\Omega_0 = [1 - u_p/u_s] \ , \qquad (3)$$

where the material is initially at rest under ambient conditions with a density ρ_0 and volume Ω_0. In a *relative* shock-wave experiment, such as the nuclear-impedance-match (NIM) experiments of concern here, only shock velocities in the sample and an adjacent reference material are measured. The mass velocity u_p and pressure P in the shocked sample are determined by impedance matching with the theoretical EOS of the reference. Density and volume may then be calculated from Eq. (3).

Previously-measured absolute Hugoniot data on Al, Cu, and Pb has been reported in the 1-10 Mbar range, using both chemical explosives[12-17]

and a two-stage light-gas gun.[18] The data on Al[12-15,18] can be utilized here to qualify our theoretical EOS for this material, as demonstrated in Fig. 2. Both experiment and theory in Al suggest a linear u_s vs. u_p relationship in this pressure range and our theoretical result is seen to be within the error bars of experiment. From the measured shock velocities in the NIM experiments[1,2] and our theoretical EOS for Al, impedance matching has been carried out to produce new Hugoniot data for seven other materials: Be, C, Fe, Cu, Mo, Pb, and SiO_2. The full elaboration of these results will be made elsewhere. We focus here on only Cu and Pb for which the corresponding theory has also been developed.

Figure 3 compares our theoretical Hugoniot for Cu with previous absolute data,[14-16,18] our impedance-matched NIM results, and one previous NIM result near 15.7 Mbar.[19] The present NIM points correspond to pressures of

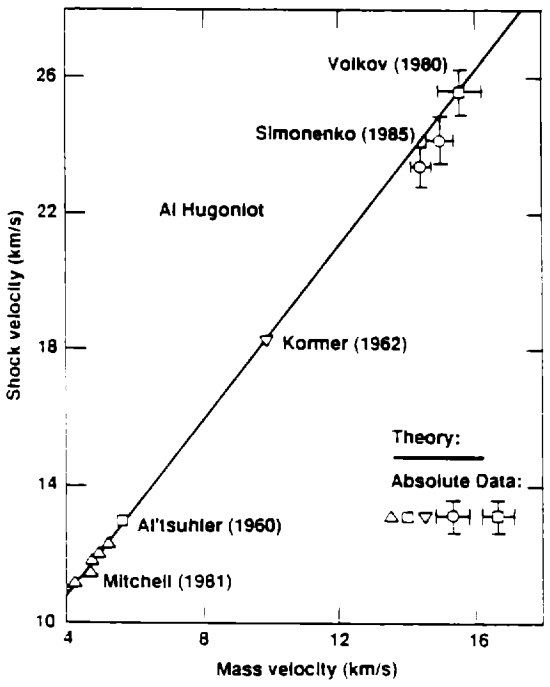

FIGURE 2
Theoretical Hugoniot for Al compared against the absolute experimental data of Refs. 12-15 and 18.

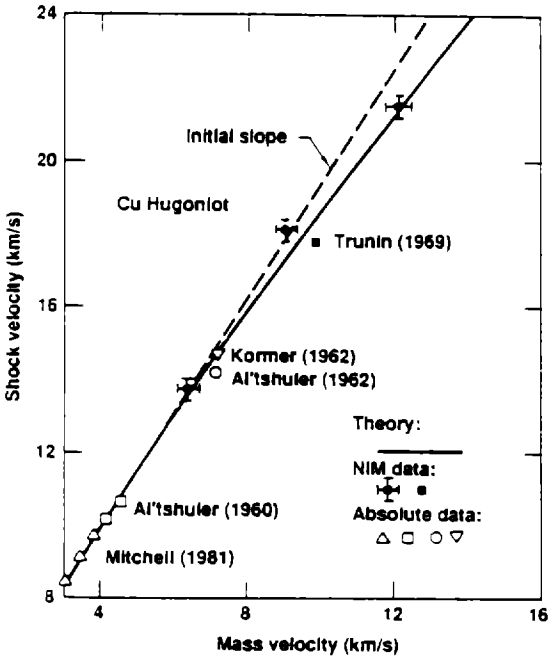

FIGURE 3
Theoretical Hugoniot for Cu compared against the experimental data of Refs. 14-16 and 18-19 and the present NIM data.

7.8, 14.7, and 23.2 Mbar. The theoretical Hugoniot is seen to be within the error bars of both the absolute data and the NIM data, except for the two points near 15 Mbar which bracket the theory on either side. Note also that the Hugoniot softens at higher pressure below its initial slope at low pressure.

The corresponding comparison is made in Fig. 4 for Pb below 10 Mbar. Here there is good agreement among the present theory, previous absolute data[15-17] and the single new NIM result at 8.9 Mbar. In fact, the latter point coincides very closely with the absolute result of Ref. 16. As in Cu, the Hugoniot is seen to soften at high pressure below its initial slope at low pressure.

It should be emphasized here that the theoretical results presented in Figs. 1-4 involve no adjustable parameters; the only input to these calculations in each case are the atomic number and mass of the element in question. The good agreement between theory

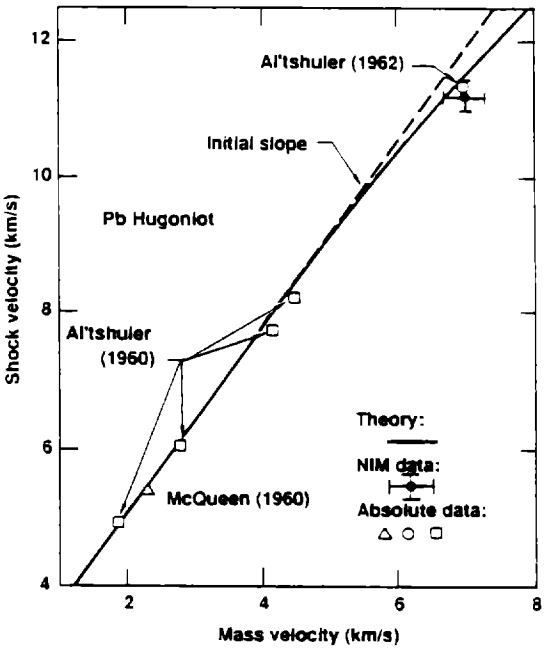

FIGURE 4
Theoretical Hugoniot for Pb compared against the absolute experimental data of Refs. 15-17 and the present NIM data.

and experiment, therefore, is significant. We believe that this agreement, together with the fact that the same theory provides an equally good description of many other physical properties of Al, Cu, and Pb,[2-5,9] lends considerable support to the validity of our equations of state away from the Hugoniot. In this regard, our theoretical results have been further applied to construct room-temperature isotherms for fcc Al, Cu, and Pb in the 1-10 Mbar range. It is proposed that these isotherms can be used as absolute pressure scales in DAC experiments in this range, as discussed in more detail in Ref. 2.

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